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The Molecular and Crystal Structure of the *p*-Bromobenzoate of an Unusual Birch Reduction Product

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It has already been found that the Birch reduction of 1,1,4aα-trimethyl-2α-hydroxy-8-methoxy-1,2,3,4,4a,9-hexahydrophenanthrene affords a tetrahydro derivative, contrary to expectations. The present paper will describe the details of the molecular structure of the unexpected reduction product, as revealed by an X-ray crystal analysis of its *p*-bromobenzoate (racemate). The crystals are triclinic, with two molecules in a unit cell of the dimensions: $a=11.155$, $b=18.123$, $c=5.912$ Å, $\alpha=94°39'$, $\beta=111°35'$, and $\gamma=90°42'$. The space group is $P\bar{1}$. The intensity measurement was made on an automatic four-circle diffractometer with Cu$K\alpha$ radiation. The structure was solved by the heavy-atom method, and was refined by the block-diagonal-matrix least-squares method, anisotropic thermal motions being assumed for all the non-hydrogen atoms. From a difference map, twenty-six of the thirty-one hydrogen atoms were also found. The final R factor was 6.5%. As a result of the present study, it has been found that the C ring of cyclohexene-type shows an unusual behavior. The length of the C–C single bond opposite to the double bond in this ring is found to be only about 1.34 Å. This remarkable shortening seems to be due to special vibrations of the two atoms concerned. The whole cyclohexene ring takes a considerably flattened, half-chair form.

It has recently been found that the reduction of I with *tert*-butyl alcohol and lithium in liquid ammonia produces a tetrahydro derivative, II (mp 162—164°C), and not the expected product, III or IV, and that the methoxyl group in the product obtained is much more reactive than those in usual allyl methyl ethers.[1] This enhanced reactivity of the methoxyl group seemed to be closely related with the conformation of the tricyclic system in the molecule. In order to obtain reliable information about the molecular conformation of II and to facilitate the understanding of the unusual chemical reactivity, an X-ray crystal analysis of its *p*-bromobenzoate (racemate) has been carried out.

Experimental

Colorless, single crystals of the racemic *p*-bromobenzoate, $C_{25}H_{31}O_3Br$, were obtained from an ether solution. Pre-

1) N. Hamanaka, T. Okuno, T. Nakajima, A. Furusaki, and T. Matsumoto, *Chem. Lett.*, in press.

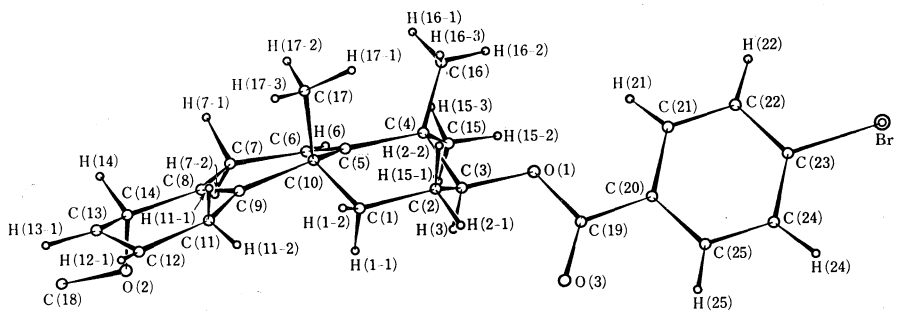
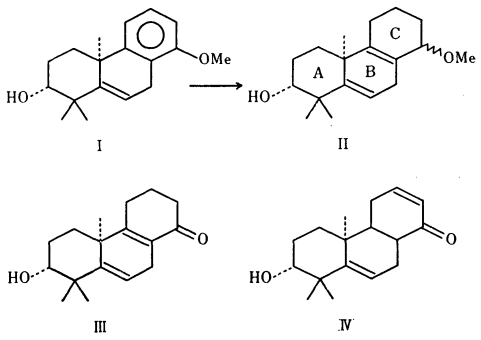


Fig. 1. The molecular framework and the numbering system of the atoms. The five hydrogen atoms which were not located in the difference map are not drawn. The absolute configuration in this picture is the inverse of those in Figs. 2, 3, and 4.



liminary photographic data and optical observations showed that the crystals were probably triclinic. The crystal data derived from diffractometer measurements are summarized in Table 1. A crystal with dimensions of about $0.1\times0.3\times0.5$ mm was sealed in a glass capillary tube and was used for the intensity measurement. The intensity data were collected with an automatic four-circle diffractometer at this University, using monochromatized Cu$K\alpha$ radiation. The intensities of the reflections with 2θ values up to 140° were measured by the ω–2θ scan technique; they were corrected for the Lorentz and polarization factors, but not for the absorption effect. In all, 3079 independent structure factors greater than $3\sigma(F)$ were obtained.

Table 1. The crystal data

Crystal system space group	Triclinic $P\bar{1}$
a	11.155±0.003 Å
b	18.123±0.003
c	5.912±0.002
α	94°39′±3′
β	111°35′±3′
γ	90°42′±3′
Z	2
D_x	1.378 g/cm³

Structure Determination

The space group was assumed to be $P\bar{1}$ throughout the present study. The position of the bromine atom was derived from a sharpened Patterson function. The first Fourier map, based on the heavy atom alone, yielded all the positions of the non-hydrogen atoms. The approximate coordinates thus obtained were first refined by the block-diagonal-matrix least-squares method, using isotropic temperature factors for all the atoms. Five cycles of the refinement reduced the value of the discrepancy factor, R, to 20.5%. Then, the least-squares refinement with anisotropic temperature factors for only the bromine atom was repeated. Consequently, it was found that the thermal parameters of the C(12) and C(13) atoms became very large (10.9 and 8.0 Å² respectively), although the R factor was decreased to 12.7%. In order to confirm the structure thus obtained, a difference synthesis was carried out, excluding five atoms: C(11), C(12), C(13), C(18), and O(2). The resulting map showed that the positions of the five atoms were all essentially correct, and that a single peak corresponded to each of these atoms. The structure thus confirmed was further refined by the least-squares method, anisotropic thermal motions being assumed for all the atoms; the R factor dropped to 8.7%. From a second difference Fourier map, twenty-six of the thirty-one hydrogen-atom positions were found. Further least-squares refinement including these hydrogen atoms reduced the R factor to 6.5%. The atomic parameters thus obtained are listed in Table 2.

All the calculations necessary for the present study were carried out on a FACOM 230—60 computer at the Computer Center of Hokkaido University.

Tables of the observed and calculated structure factors are preserved by the Chemical Society of Japan.

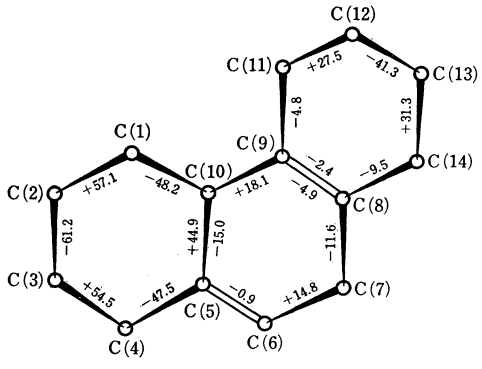


Fig. 2. The torsion angles for the tricyclic system (in degrees).

TABLE 2. THE FINAL ATOMIC PARAMETERS WITH THEIR STANDARD DEVIATIONS

(a) The non-hydrogen atoms

The parameters are multiplied by 10^4.

(1) The fractional coordinates

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Br	1747.9(7)	8714.6(3)	2955.5(15)	C (12)	4766(7)	972(4)	7677(24)
O (1)	2749(4)	5094(1)	4763(6)	C (13)	3744(7)	492(4)	6884(22)
O (2)	2018(6)	851(2)	8332(9)	C (14)	2439(5)	802(2)	6347(10)
O (3)	3308(5)	5525(2)	8679(7)	C (15)	497(5)	4155(3)	3747(10)
C (1)	4313(4)	3269(2)	6110(9)	C (16)	1604(5)	3994(2)	839(8)
C (2)	4176(5)	4067(2)	5440(9)	C (17)	3420(6)	2562(3)	1916(10)
C (3)	2882(5)	4325(2)	5372(8)	C (18)	1553(8)	175(4)	8814(16)
C (4)	1725(4)	3874(2)	3473(8)	C (19)	2963(4)	5629(2)	6568(8)
C (5)	1922(4)	3049(2)	3982(7)	C (20)	2677(4)	6369(2)	5631(8)
C (6)	945(4)	2636(2)	4066(9)	C (21)	2116(5)	6455(2)	3157(9)
C (7)	1003(5)	1835(3)	4494(12)	C (22)	1819(5)	7153(2)	2375(10)
C (8)	2342(4)	1572(2)	5453(9)	C (23)	2121(4)	7761(2)	4083(10)
C (9)	3354(4)	1972(2)	5494(8)	C (24)	2683(5)	7690(2)	6530(10)
C (10)	3229(4)	2721(2)	4370(8)	C (25)	2954(5)	6987(2)	7297(9)
C (11)	4689(5)	1684(3)	6548(13)				

(2) The anisotropic temperature factors

These are expressed as

$$\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{23}kl+\beta_{31}lh)\right].$$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{23}	β_{31}
Br	159.6(7)	24.1(1)	727.7(32)	22.4(4)	102.5(10)	305.0(24)
O (1)	150(4)	20(1)	249(11)	4(3)	28(5)	159(11)
O (2)	285(8)	30(1)	532(19)	−11(5)	71(7)	429(21)
O (3)	241(7)	29(1)	249(12)	12(4)	23(6)	105(15)
C (1)	86(4)	24(1)	353(18)	1(4)	45(7)	110(15)
C (2)	102(5)	25(1)	385(19)	−18(4)	28(8)	120(16)
C (3)	115(5)	20(1)	265(15)	2(3)	34(6)	138(14)
C (4)	96(4)	24(1)	219(14)	9(4)	35(6)	109(13)
C (5)	82(4)	23(1)	216(14)	4(3)	27(6)	100(13)
C (6)	80(4)	32(1)	381(19)	7(4)	83(8)	104(15)
C (7)	89(5)	33(1)	618(28)	−8(4)	125(11)	112(19)
C (8)	88(4)	21(1)	338(17)	7(3)	42(7)	99(14)
C (9)	87(4)	23(1)	295(16)	8(3)	25(7)	117(14)
C (10)	77(4)	22(1)	287(16)	4(3)	25(6)	133(13)
C (11)	101(5)	29(1)	705(31)	18(4)	88(11)	236(21)
C (12)	113(7)	44(2)	1819(86)	68(7)	345(24)	376(39)
C (13)	140(8)	38(2)	1561(73)	37(6)	330(21)	297(38)
C (14)	112(5)	24(1)	438(21)	−7(4)	61(8)	137(17)
C (15)	107(5)	31(1)	416(21)	25(4)	63(9)	193(17)
C (16)	126(6)	29(1)	235(15)	5(4)	47(7)	120(15)
C (17)	142(6)	34(2)	368(20)	14(5)	21(9)	271(19)
C (18)	220(10)	42(2)	759(38)	7(7)	181(15)	392(33)
C (19)	91(5)	25(1)	286(16)	−2(4)	17(7)	106(14)
C (20)	71(4)	22(1)	312(17)	−4(3)	9(7)	98(13)
C (21)	135(6)	23(1)	306(17)	−5(4)	9(7)	149(17)
C (22)	138(6)	27(1)	363(20)	10(4)	46(8)	159(18)
C (23)	85(4)	20(1)	535(23)	4(3)	65(8)	199(17)
C (24)	131(6)	24(1)	421(22)	−2(4)	−9(8)	159(18)
C (25)	98(5)	26(1)	322(18)	−4(4)	−18(8)	68(15)

(b) The hydrogen atoms

The positional and thermal parameters are multiplied by 10^3 and 10 respectively.

Atom	x/a	y/b	z/c	B
H (1-1)	424 (4)	326 (2)	763 (8)	10 (8)
H (1-2)	511 (6)	309 (3)	608 (11)	31 (12)
H (2-1)	482 (5)	436 (3)	670 (10)	23 (10)
H (2-2)	431 (6)	405 (3)	385 (11)	34 (12)
H (3)	280 (6)	429 (3)	687 (11)	31 (12)
H (6)	9 (4)	284 (2)	385 (9)	13 (9)
H (7-1)	52 (6)	154 (3)	288 (11)	29 (12)
H (7-2)	57 (7)	172 (4)	565 (14)	50 (16)
H (11-1)	501 (7)	166 (4)	543 (13)	43 (14)
H (11-2)	529 (6)	201 (3)	748 (11)	29 (11)
H (12-1)	554 (5)	79 (3)	798 (11)	25 (11)
H (13-1)	382 (6)	−3 (3)	743 (12)	35 (12)
H (14)	176 (5)	47 (3)	497 (11)	26 (11)
H (15-1)	41 (7)	409 (4)	512 (13)	45 (15)
H (15-2)	40 (4)	467 (2)	350 (9)	12 (9)
H (15-3)	−34 (5)	391 (3)	249 (10)	20 (10)
H (16-1)	100 (6)	365 (3)	−23 (11)	30 (12)
H (16-2)	133 (5)	445 (3)	49 (10)	23 (10)
H (16-3)	240 (5)	397 (3)	66 (9)	17 (9)
H (17-1)	343 (5)	303 (3)	119 (10)	23 (10)
H (17-2)	275 (6)	233 (3)	80 (11)	32 (12)
H (17-3)	415 (8)	226 (5)	217 (16)	62 (18)
H (21)	197 (5)	602 (3)	217 (10)	19 (9)
H (22)	139 (6)	723 (4)	74 (13)	39 (14)
H (24)	289 (6)	816 (3)	765 (11)	31 (12)
H (25)	338 (5)	695 (3)	899 (11)	27 (11)

Results and Discussion

The molecular framework thus obtained and the torsion angles for the A, B, and C rings are shown in Figs. 1 and 2 respectively. As will be seen in these figures, the C ring takes a considerably flattened half-chair form, with the methoxyl group, O(2)–C(18)H_3, placed in the axial position and on the opposite side of the mean plane of the molecule to the C(17) atom, while the A ring has a distorted chair form, with the O(1) atom in the equatorial position. On the other hand, the B ring containing two endocyclic double bonds exists in the boat conformation. The bond distances and angles, along with their estimated standard deviations, are given in Tables 3 and 4 respectively. The correction for the thermal motion was made on the assumption of a riding motion by means of the Busing-Levy method.[2] Considering their standard deviations, these values are all reasonable except for the C(12)–C(13) bond. The unusual behavior of this bond will be described in detail later.

The chair form of the A ring is somewhat distorted, as has been described above. This may be mainly due to the fusion of the B ring, but it may be partly due to the repulsion between the two axial methyl groups, C(16)H_3 and C(17)H_3. As will be seen in Fig. 2, the A ring is less puckered than the normal chair-shaped ring of cyclohexane. From the average valence angle in the ring, 112.2°, the average torsion angle is estimated to be 52.6° by using Altona's equation.[3] This value is in good agreement with the average of the six observed torsion angles, 52.2°. The conformations of the three methyl groups in the A ring are shown in Fig. 3. In order to avoid a closer approach of the H(16–3) and H(17–1) atoms, neither the C(16)-H_3 nor C(17)H_3 methyl group takes the ideal staggered conformation; the deviations are about 13° and 10° respectively. Thus, the H(16–3) and H(17–1) atoms maintain a distance of about 2.05 Å. On the other hand, the conformation of the equatorial C(15)H_3 group around the C(15)–C(4) bond also deviates by

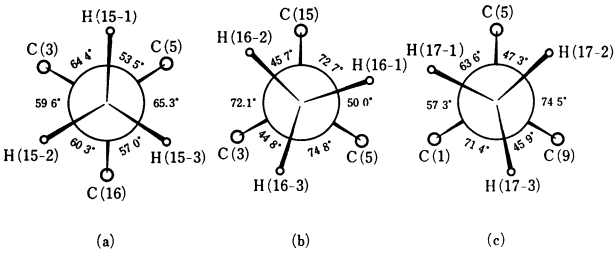


Fig. 3. The Newman projections along the bonds, (a) C (4)-C(15), (b) C(4)-C(16), and (c) C(10)-C(17).

2) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **17**, 142 (1964).

3) C. Altona, H. J. Geise, and C. Romers, *Rec. Trav. Chim.*, **85**, 1197 (1966).

Table 3. The bond distances with their standard deviations

(a) The bond distances between the non-hydrogen atoms
The distances corrected for the thermal motion are given in parentheses

Bond	Distance	σ	Bond	Distance	σ
C (1) - C (2)	1.526 (1.530)	0.006	C (10) - C (17)	1.548 (1.566)	0.008
C (1) - C (10)	1.548 (1.554)	0.005	C (11) - C (12)	1.490 (1.554)	0.011
C (2) - C (3)	1.510 (1.517)	0.007	C (12) - C (13)	1.340 (1.347)	0.010
C (3) - C (4)	1.535 (1.537)	0.005	C (13) - C (14)	1.498 (1.566)	0.009
C (3) - O (1)	1.462 (1.468)	0.005	C (14) - O (2)	1.413 (1.448)	0.009
C (4) - C (5)	1.550 (1.553)	0.005	C (18) - O (2)	1.414 (1.420)	0.009
C (4) - C (15)	1.526 (1.540)	0.008	C (19) - C (20)	1.486 (1.489)	0.006
C (4) - C (16)	1.547 (1.556)	0.007	C (19) - O (1)	1.332 (1.340)	0.005
C (5) - C (6)	1.333 (1.347)	0.007	C (19) - O (3)	1.195 (1.236)	0.006
C (5) - C (10)	1.527 (1.529)	0.006	C (20) - C (21)	1.386 (1.399)	0.007
C (6) - C (7)	1.491 (1.507)	0.007	C (20) - C (25)	1.382 (1.394)	0.006
C (7) - C (8)	1.490 (1.509)	0.007	C (21) - C (22)	1.383 (1.389)	0.006
C (8) - C (9)	1.325 (1.328)	0.007	C (22) - C (23)	1.382 (1.392)	0.006
C (8) - C (14)	1.523 (1.533)	0.006	C (23) - C (24)	1.367 (1.379)	0.008
C (9) - C (10)	1.545 (1.547)	0.006	C (23) - Br	1.898 (1.916)	0.004
C (9) - C (11)	1.506 (1.528)	0.007	C (24) - C (25)	1.386 (1.395)	0.006

(b) The bond distances involving the hydrogen atoms

Bond	D	σ	Bond	D	σ
C (1) - H (1-1)	0.93	0.05	C (15) - H (15-1)	0.87	0.09
C (1) - H (1-2)	0.96	0.07	C (15) - H (15-2)	0.97	0.05
C (2) - H (2-1)	0.94	0.05	C (15) - H (15-3)	1.02	0.05
C (2) - H (2-2)	1.00	0.07	C (16) - H (16-1)	0.93	0.05
C (3) - H (3)	0.93	0.07	C (16) - H (16-2)	0.90	0.05
C (6) - H (6)	1.00	0.05	C (16) - H (16-3)	0.93	0.06
C (7) - H (7-1)	1.01	0.06	C (17) - H (17-1)	0.99	0.06
C (7) - H (7-2)	1.01	0.10	C (17) - H (17-2)	0.87	0.05
C (11) - H (11-1)	0.86	0.09	C (17) - H (17-3)	0.96	0.09
C (11) - H (11-2)	0.88	0.05	C (21) - H (21)	0.91	0.05
C (12) - H (12-1)	0.88	0.06	C (22) - H (22)	0.93	0.07
C (13) - H (13-1)	1.01	0.06	C (24) - H (24)	1.00	0.06
C (14) - H (14)	1.03	0.05	C (25) - H (25)	0.95	0.06

about 3° from the ideal staggered conformation. The distance of the H(15-3) atom from the H(6) atom is about 2.14 Å.

The B ring contains two non-conjugated double bonds, C(5)=C(6) and C(8)=C(9). The latter double bond is somewhat twisted, although the former holds a good planarity. The deviations of the atoms from the least-squares best plane through the C(7), C(8), C(9), C(10), C(11), and C(14) atoms are given in Table 5. The angle of twisting around the C(8)=C(9) bond is estimated to be about 3.7° by averaging the torsion angles, C(7)–C(8)–C(9)–C(10) and C(14)–C(8)–C(9)–C(11). The angle between the above best plane and the least-squares plane through the C(4), C(5), C(6), C(7), and C(10) atoms is about 15.1°.

The C ring is the most interesting part of the present molecule, since it seems to have a close relation to the high reactivity of the methoxyl group. The conformation and dimensions of this ring are shown in Fig. 4. This figure includes three remarkable features. The first is that the length of the C(12)–C(13) bond, 1.340±0.010 Å, is too short for a C–C single bond, and that the C–C–C valence angles at the C(12) and C(13) atoms, 119.7±0.6° and 117.5±0.7°, are too large for tetrahedral valence angles. Judging from these dimensions alone, the C(12)–C(13) bond must be a C=C double bond. However, both elemental analysis and NMR spectrum demonstrate that the C(12) and C(13) atoms form a single bond.[1] The second is that the C(12) and C(13) atoms vibrate vigorously in a direction almost perpendicular to the mean plane of the C ring. The root-mean-square deviations and direction cosines in the principal axes of the thermal ellipsoids are given in Table 6. The largest root-mean-square deviations for the C(12) and C(13) atoms are no less than about 0.55 and 0.52 Å respectively. Even though the C(12)–C(13) bond distance is corrected for these large thermal motions, the correction is only about 0.007 Å as long as the riding motion is assumed. However, if the highly-correlated antiparallel motion is assumed for the two atoms, the corrected distance amounts to about 1.73 Å. Accordingly, the shortening of the C(12)–C(13) single bond might be explained by such a thermal motion effect, but it

TABLE 4. THE BOND ANGLES WITH THEIR STANDARD DEVIATIONS

	Angle	σ		Angle	σ
C (2) - C (1) - C (10)	114.3	0.3	C (1) - C (2) - H (2-1)	107	3
C (1) - C (2) - C (3)	108.9	0.4	C (1) - C (2) - H (2-2)	105	4
C (2) - C (3) - C (4)	114.0	0.4	C (3) - C (2) - H (2-1)	108	3
C (2) - C (3) - O (1)	109.3	0.4	C (3) - C (2) - H (2-2)	115	4
C (4) - C (3) - O (1)	106.9	0.3	H (2-1) - C (2) - H (2-2)	112	5
C (3) - C (4) - C (5)	107.0	0.3	C (2) - C (3) - H (3)	111	4
C (3) - C (4) - C (15)	108.2	0.4	C (4) - C (3) - H (3)	106	4
C (3) - C (4) - C (16)	111.4	0.4	O (1) - C (3) - H (3)	110	4
C (5) - C (4) - C (15)	112.2	0.4	C (5) - C (6) - H (6)	122	3
C (5) - C (4) - C (16)	111.5	0.4	C (7) - C (6) - H (6)	113	3
C (15) - C (4) - C (16)	106.5	0.4	C (6) - C (7) - H (7-1)	108	3
C (4) - C (5) - C (6)	119.5	0.4	C (6) - C (7) - H (7-2)	112	5
C (4) - C (5) - C (10)	119.6	0.3	C (8) - C (7) - H (7-1)	108	3
C (6) - C (5) - C (10)	120.9	0.4	C (8) - C (7) - H (7-2)	108	5
C (5) - C (6) - C (7)	124.7	0.5	H (7-1) - C (7) - H (7-2)	107	6
C (6) - C (7) - C (8)	113.4	0.4	C (9) - C (11) - H (11-1)	108	6
C (7) - C (8) - C (9)	122.7	0.4	C (9) - C (11) - H (11-2)	116	3
C (7) - C (8) - C (14)	114.1	0.4	C (12) - C (11) - H (11-1)	112	6
C (9) - C (8) - C (14)	123.2	0.4	C (12) - C (11) - H (11-2)	112	3
C (8) - C (9) - C (10)	122.7	0.4	H (11-1) - C 11) - H (11-2)	92	7
C (8) - C (9) - C (11)	120.2	0.4	C (11) - C (12) - H (12-1)	110	4
C (10) - C (9) - C (11)	117.0	0.3	C (13) - C (12) - H (12-1)	118	4
C (1) - C (10) - C (5)	109.2	0.3	C (12) - C (13) - H (13-1)	121	4
C (1) - C (10) - C (9)	108.7	0.3	C (14) - C (13) - H (13-1)	114	4
C (1) - C (10) - C (17)	109.9	0.4	C (8) - C (14) - H (14)	106	3
C (5) - C (10) - (9)	111.8	0.4	C (13) - C (14) - H (14)	109	3
C (5) - C (10) - C (17)	111.1	0.4	O (2) - C (14) - H (14)	106	3
C (9) - C (10) - C (17)	106.1	0.4	C (4) - C (15) - H (15-1)	116	6
C (9) - C (11) - C (12)	115.1	0.6	C (4) - C (15) - H (15-2)	112	3
C (11) - C (12) - C (13)	119.7	0.6	C (4) - C (15) - H (15-3)	114	3
C (12) - C (13) - C (14)	117.5	0.7	H (15-1) - C (15) - H (15-2)	107	6
C (8) - C (14) - C (13)	113.3	0.4	H (15-1) - C (15) - H (15-3)	102	6
C (8) - C (14) - O (2)	106.5	0.4	H (15-2) - C (15) - H (15-3)	104	4
C (13) - C (14) - O (2)	114.8	0.5	C (4) - C (16) - H (16-1)	109	3
C (20) - C (19) - O (1)	111.8	0.4	C (4) - C (16) - H (16-2)	110	3
C (20) - C (19) - O (3)	124.0	0.4	C (4) - C (16) - H (16-3)	112	4
O (1) - C (19) - O (3)	124.2	0.4	H (16-1) - C (16) - H (16-2)	108	5
C (19) - C (20) - C (21)	122.2	0.4	H (16-1) - C (16) - H (16-3)	113	5
C (19) - C (20) - C (25)	118.5	0.4	H (16-2) - C (16) - H (16-3)	106	5
C (21) - C (20) - C (25)	119.3	0.4	C (10) - C (17) - H (17-1)	110	3
C (20) - C (21) - C (22)	120.2	0.4	C (10) - C (17) - H (17-2)	112	4
C (21) - C (22) - C (23)	119.2	0.5	C (10) - C (17) - H (17-3)	109	5
C (22) - C (23) - C (24)	121.6	0.4	H (17-1) - C (17) - H (17-2)	101	5
C (22) - C (23) - Br	118.4	0.4	H (17-1) - C (17) - H (17-3)	117	6
C (24) - C (23) - Br	120.0	0.4	C (17-2) - C (17) - H (17-3)	109	6
C (23) - C (24) - C (25)	118.7	0.4	C (20) - C (21) - H (21)	114	3
C (20) - C (25) - C (24)	121.0	0.4	C (22) - C (21) - H (21)	126	3
C (3) - O (1) - C (19)	118.4	0.3	C (21) - C (22) - H (22)	123	4
C (14) - O (2) - C (18)	115.2	0.5	C (23) - C (22) - H (22)	118	4
C (2) - C (1) - H (1-1)	108	3	C (23) - C (24) - H (24)	117	3
C (2) - C (1) - H (1-2)	110	4	C (25) - C (24) - H (24)	124	3
C (10) - C (1) - H (1-1)	105	3	C (24) - C (25) - H (25)	117	3
C (10) - C (1) - H (1-2)	106	4	C (20) - C (25) - H (25)	122	3
H (1-1) - C (1)) H (1-2)	113	5			

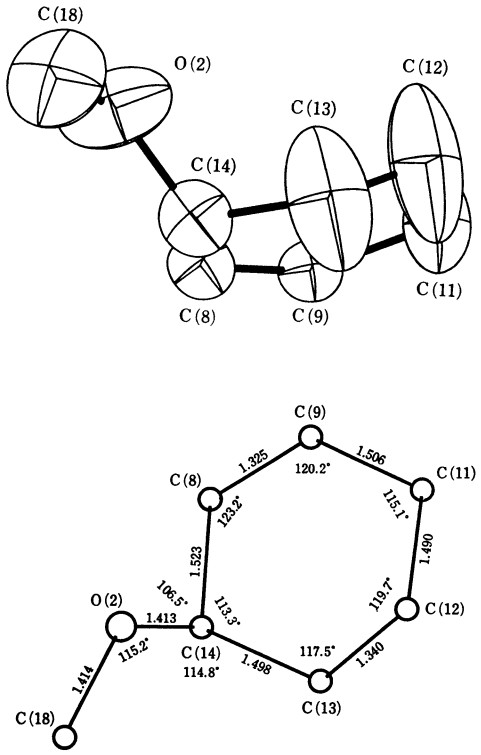


Fig. 4. The conformation and dimensions of the C ring. The thermal ellipsoids are scaled to enclose 50% probability.

seems to be difficult at the present stage to answer the question why these two atoms vibrate vigorously in a direction nearly antiparallel to each other. On the other hand, if this remarkable anisotropy of thermal motion were due to some disordering associated with the conformation of the C ring, the electron density distribution would afford double peaks for the C(12) and C(13) atoms, since the separation between two possible

Table 5. The deviations from the least-squares plane through the C(7), C(8), C(9), C(10), C(11), and C(14) atoms

Atom	Deviation	Atom	Deviation
C (7)	+0.035 Å	C (11)	+0.031 Å
C (8)	+0.010	C (14)	−0.048
C (9)	+0.021	C (5)	+0.311
C (10)	−0.049	C (6)	+0.348

positions is estimated to be about 0.76 Å from the observed distance for the C(12)–C(13) single bond. However, in fact, the difference map calculated excluding these atoms gave single peaks to them, as has been already mentioned in the section of Structure Determination. Hence, it seems to be unreasonable to think that the unusual behavior of the two atoms is to be explained by such a disordering. The third feature is that the methoxyl group is not in the equatorial position, but in the axial position, and that the half-chair form of the C ring is considerably more flattened than those in many other substances containing a cyclohexene ring.[4] The deviations from the least-squares best plane through the C(8), C(9), C(11), and C(14) atoms are no more than about 0.17 and 0.28 Å for the C(12) and C(13) atoms respectively; these values are considerably smaller than those found in cyclohexene, ±0.3673 Å.[5] One of the important factors which control the conformation of the C ring might be the H(1–2)···H(11–2) interaction, since the distance between the two hydrogen atoms, 2.17 Å, varies sensitively with the conformational change of the C ring. The methoxyl carbon atom, C(18), is placed at such a position that the O(2)–C(18) bond makes azimuthal angles of about 156.2° and 77.6° with the C(8)–C(14) and C(13)–C(14) bonds around the C(14)–O(2) bond respectively. It is interesting

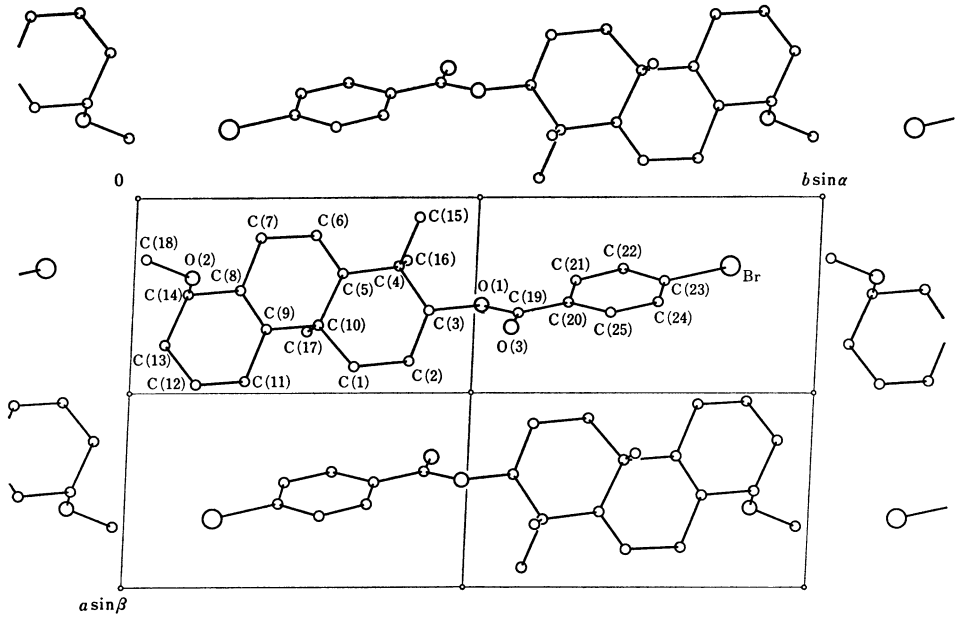


Fig. 5. The crystal structure viewed along the *c* axis.

4) B. Koch, *Acta Crystallogr.*, **B28**, 1151 (1972).

Table 6. The root-mean-square deviations and direction cosines in the principal axes of the thermal ellipsoids

$B_i = 8\pi^2 u_i^2$ where u_i is the root-mean-square deviation corresponding to the ith axis of the ellipsoid. C_{ia}, C_{ib}, and C_{ic} are the direction cosines of the i axis with respect to the orthogonal coordinate axes by $\boldsymbol{b}\times\boldsymbol{c}^*$, $\boldsymbol{b}$, and $\boldsymbol{c}^*$.

Atom	Axis i	B_i	u_i	C_{ia}	C_{ib}	C_{ic}
C (8)	1	2.55	0.180	0.050	−0.952	0.303
	2	3.71	0.217	0.771	0.229	0.594
	3	4.52	0.239	0.635	−0.204	−0.745
C (9)	1	2.91	0.192	0.073	−0.967	0.245
	2	3.57	0.213	−0.215	0.225	0.950
	3	3.74	0.218	−0.974	−0.122	−0.191
C (11)	1	3.33	0.205	0.169	−0.965	0.199
	2	4.02	0.226	0.981	0.185	0.066
	3	8.68	0.332	0.100	−0.184	−0.978
C (12)	1	2.55	0.180	−0.537	0.783	−0.313
	2	5.50	0.264	0.818	0.574	0.033
	3	23.91	0.550	0.206	−0.238	−0.949
C (13)	1	2.46	0.177	−0.082	0.949	−0.304
	2	5.98	0.275	0.961	0.156	0.229
	3	21.24	0.519	0.265	−0.273	−0.925
C (14)	1	2.57	0.180	−0.260	−0.941	0.217
	2	4.75	0.245	0.735	−0.047	0.676
	3	5.98	0.275	−0.626	0.335	0.704
O (2)	1	2.90	0.192	−0.284	−0.865	0.415
	2	5.88	0.273	−0.296	0.491	0.820
	3	12.38	0.396	−0.912	0.110	−0.395
C (18)	1	3.04	0.196	−0.302	−0.845	0.441
	2	8.99	0.338	0.917	−0.385	−0.109
	3	10.58	0.366	−0.262	−0.371	−0.891

Table 7. The principal intermolecular distances

(1) I···II (III···I)		(4) I···VIII (VIII···I)		
Br···C (13)	3.94 Å	C (15)···C (15)	3.66 Å	
(2) I···IV (V···I)		C (15)···C (19)	3.82	
O (2)···C (17)	3.60 Å	C (15)···C (20)	3.81	
O (3)···C (21)	3.68	(5) I···IX (IX···I)		
C (8)···C (17)	3.84	Br···C (11)	3.96 Å	
C (9)···C (17)	3.83	C (1)···C (21)	3.87	
C (15)···C (16)	3.95	C (2)···C (2)	3.99	
C (25)···C (22)	3.66	C (2)···C (19)	3.84	
(3) I···VI (VII···I)		C (2)···C (20)	3.87	
Br···C (18)	3.70 Å	C (11)···C (23)	3.84	

I: x/a, y/b, z/c (given in Table 2). II: x/a, $1+y/b$, z/c. III: x/a, $-1+y/b$, z/c. IV: x/a, y/b, $1+z/c$. V: x/a, y/b, $-1+z/c$. VI: x/a, $1+y/b$, $-1+z/c$. VII: x/a, $-1+y/b$, $1+z/c$. VIII: $-x/a$, $1-y/b$, $1-z/c$. IX: $1-x/a$, $1-y/b$, $1-z/c$.

to note in Fig. 4 that the O(2) atom as well as the C(13) atom vibrates rotationally with the C(8)–C(14) bond as an axis of rotation. It has already been mentioned that the five hydrogen atoms could not be found in the difference Fourier map. Three of them are methoxyl hydrogen atoms, and the remaining two are axial ones at the C(12) and C(13) atoms. It seems at first sight strange that only the equatorial hydrogen atoms at the C(12) and C(13) atoms can be located, notwithstanding the large thermal motions of these two carbon atoms. This may be explained by taking it into consideration that, since, in the cyclohexene molecule, the equatorial hydrogen atoms at the C(12) and C(13) atoms deviate by only about 0.10 Å from the double-bond plane,[5] there are always equatorial hydrogen atoms in the neighborhood of the double-bond plane even if the α and β hydrogen atoms exchange the axial and equatorial positions with each other by a flipping of the ring.

The *p*-bromobenzoate group is not planar as a whole, but the carboxylate group is twisted at an angle of about 7.1° from the benzene-ring plane. The C(3) and O(3) atoms also deviate by about 3.2° from the eclipsed conformation around the O(1)–C(19) bond. On the other hand, the benzoyl group takes roughly the *cis* conformation with the H(3) atom around the O(1)–C(3) bond; the deviation from the ideal *cis* conformation is about 21°. Consequently, the O(3) atom is situated at a very small distance (about 2.36 Å) from the H(3) atom. This suggests that these two atoms exert a stronger attractive force on each other than the usual van der Waals interaction.

The molecular arrangement viewed along the *c* axis is shown in Fig. 5. The principal intermolecular distances are listed in Table 7. The molecules are connected mainly by the usual van der Waals interactions.

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5) J. F. Chiang and S. H. Bauer, *J. Amer. Chem. Soc.*, **91**, 1898 (1969).